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13. ABSTRACT *(Maximum 200 Words)*

The goal of this exploratory program was to investigate the possibility to form electrosprays of water and other volatile materials in a vacuum, by (1) either coating the Taylor cone of water with an involatile liquid or (2) by minimizing the tip diameter. Approach (2) was followed only to a limited degree in collaboration with Professor Barrero. Bare Taylor cones of water can be stabilized in vacuo, but this second method was considered less promising than the first, and not pursued further. Method (1) has proven successful in highly conducting water electrolytes surrounded by a thin layer of diffusion pump oil, and has worked similarly with formamide solutions. The viability of this approach has therefore been demonstrated. Liquid feed systems based on commercial capillaries have limited the possibility to finely control the flow rate of oil. A new oil-feed technique based on pulling the end of the outer capillary into a slightly conical shape whose exit ID fits exactly with the exit OD of the inner capillary has been designed. It should provide a much better oil flow control, but it remains to be exploited systematically

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1. INTRODUCTION

Our proposal noted the important advantages offered by water as a colloidal propellant, based on the formation of eletrified liquid cones (Taylor cones) in a vacuum. We offered two approaches to overcome the problem associated with the high volatility of water. Subsequently, the interest of this research has increased as a result of two circumstances of which we were not aware at the time of submission. First, water has strategic interest as a space propellant as there are plans to make it available in space. Second, all propellants other than ionic liquids having shown good properties for colloidal propulsion turn out to be sufficiently volatile to limit their use in space under conditions of high specific impulse. Formamide is a clear example of this. The approach offered in our proposal to deal with water can be used similarly with formamide and other moderately volatile propellants. Furthermore, the use of an oil sheath to avoid liquid evaporation becames particularly attractive during long periods of propulsive inactivity.

2. Progress made

2.1 Miniaturized sources. We still consider this approach as promising as indicated in our original proposal. However, because it began to be investigated by two other groups shortly after this project was funded, we decided not to duplicate efforts. We will hence report only on the related results from these two other groups. First, Lozano and Martinez-Sanchez (2002) have succeeded at running Taylor cones of formamide from capillary tubes with 5 μm bores. On the assumption that their tips are sharpened to this ID, this implies a substantial improvement over our 20 μm tips (16 times less evoparative losses). Their study remains to be reported in detail, but they have attained considerably smaller flow rates than earlier work (Gamero and Hruby, 2001; Bocanegra et al., 2002), with interesting associated performance improvements. Most relevant to our project is the fact that such small capillaries can be operated for hours without clogging problems.

Professor Antonio Barrero and his colleagues in Seville have also succeeded at spraying water in a vacuum from small tips, though not as small as indicated in our proposal (7 μm). They have photographed conical tips where a substantial fraction of the cone was frozen, but the tip region remained liquid and projected a steady current.

2.2 Electrosprays of coaxial liquids

In this approach evaporation is avoided by covering the Taylor cone of a volatile liquid by a coaxial layer of an involatile substance. Hence, the inner liquid can be chosen according to its desired physical properties (electrical conductivity and viscosity) irrespective of its volatility, while the sheathing liquid is selected based on its volatility, with little concern for electrical conductivity. This represents a tremendous advantage, because most solvents of modest viscosity whose electrolytes can yield high electrical conductivities have high volatility, while most liquids having low vapor pressure are either too viscous or not sufficiently polar to be good solvents of salts. Decoupling these two types of properties enables a vastly larger range of Taylor cone combinations than previously available with single liquids.

Mr. Ismael Guerrero did assemble a vacuum system evacuated just with a mechanical pump producing a vacuum level of several tens of millitor. This was sufficient for our exploratory purposes, although it would not be adequate for mass spectrometric characterization of the particles produced. He performed initial experiments to develop an electrospray source able to feed two concentric liquids at flow rates in the range of 10^{-8} cm^3/s, which is many orders of magnitude smaller than previously achieved in the pioneering work of Professor Barrero and colleagues. The low flow rates quoted are nonetheless essential in order to attain the levels of specific impulse necessary for water to be of interest as a colloidal propellant.

We did identify early on a serious technical problem associated to the control of the outer flow rate of oil. In essence, one must combine two capillary tubes where the ID of the outer tube matches closely the ID of the inner one. Given that the OD of the only commercially available capillaries having the necessary IDs of 20 μm (or less) is as large as 150 μm, the gap between both capillaries needs to be of some 10 μm or less (larger gaps lead to too large flow rates of the outer liquid). Unfortunately the best match commercially available is ID 150 μm, OD 177 μm, with tolerances of up to 10 μm. All our preliminary work was therefore carried out with this relatively large gap. We have managed to control oil flow rates by adding large flow resistances in the oil feed line upstream of the annular region between the two capillaries. The main associated problem is that it takes a very long time to fill the relatively large volume in the annular region by means of the low flow rate supplied through the large resistor upstream of it. This arrangement is therefore rather impractical for carrying systematic studies. However, it has served well for studying a few flows and obtain highly valuable qualitative information. The rate of progress has, however, been rather slow as a result of this large fill-time limitation.

Our most interesting and conclusive results were obtained during the month of August/2002 through the visit of Dr. I. Aguirre. By shifting from metal to silica for the outer tube, he identified the additional serious problem that the two capillaries are never concentric. Rather, one is almost touching the other on one side, while the opposite side has twice the average gap (figure 1). This lack of axial symmetry leads to a considerably smaller flow resistance than predicted for an axisymmetric situation. In addition, capillary forces tend to draw the liquid into the narrow gap region, leaving the large-gap region prone to be filled by air (or vacuum). As a result, it is rather difficult to attain steady state conditions. Even when there is no active supply of oil from the reservoir, the inner Taylor cone tends to entrain oil from the wide gap side of the annular region, which is then slowly "filled by vacuum".

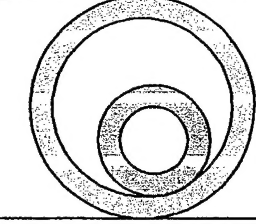

Figure 1. Sketch of capillary off-centering problem

In spite of these challenges, Dr. Aguirre armed himself with patience, and was able to achieve stable flows for long periods of time. During these periods he has investigated several highly conducting electrolytes of water and formamide, containing salts at concentrations from 0.1 M to almost 2 M. In all cases his outer sheath liquid was of Neovac SY diffusion pump fluid (from Varian, Lexington, Mass), with a room temperature viscosity coefficient of 45 cp. In particular, he was able to control oil-coated water Taylor cones in vacuum at flow rates around 2.10^{-8} ml/s of oil flow and $26.\ 10^{-8}$ ml/s of water flow, with relatively small electrical current variations for periods of over 90 minutes. This shows inequivocally that the perceived problem that water would tend to boil does not arise in practice, and that the proposed mode of operation is accessible to experiment.

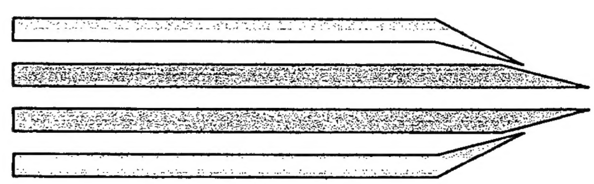

Figure 2: Sketch of the improved coaxial capillary design, with a pulled outer capillary and a sharpened inner capillary, where flow resistance is maximized at the outlet and centering is achieved automatically

These results are of great interest, as they show the viability of colloidal propulsion based on coaxial flows at high electrical conductivities and small flow rates. However, before one can embark on a systematic study of the propulsion characteristics of such binary colloidal systems,

it is essential to design a feed system with a perfectly stable oil flow rate, and with fill and stabilization times of minutes rather than hours. During the last week of Dr. Aguirre's one-month stay we were able to design and build such a system. The approach is still dependent on a lot of manual skill, and requires several hours of patient work. But once the source is made it can operate for hundreds of hours. The new oil injector reduces drastically the fill time, yet increases flow resistance by placing the largest flow restriction at the end of the capillary, rather than at the beginning. This is done by using a silica capillary for the outer flow, which is previously pulled under a torch to reduce its diameter to less than 150 μm. We then sharpen the tip region of the 150 μm inner OD into a cone of small included angle, and introduce it inside the outer capillary until it touches the pulled conical region of the outer capillary. We then cut the outer capillary at this point under the microscope, polish it, and patiently arrive to a condition where the inner needle protrudes slightly outside of the outer one, while the gap between both is almost zero. The inner capillary is then pulled back slightly to leave a small opening (figure 2). The result is not only that the flow resistance is greatly augmented and the fill time greatly diminished. In addition, the centering of the two capillaries in their tip region is almost perfect, eliminating the problem previously encountered of the appearance of air or vacuum cavities on the annular region between the capillaries. We have built successfully two prototypes of these emitters. The first was prone to breakup due to the fragility of the outer capillary and the presence of tensions in the feed line. A second design free from such tensions has been implemented, and demonstrated adequate structural characteristics. Although the final setup is much better from flow control and structural considerations than its predecessors, it remains to be tested systematically. We believe the new feed system should enable moving into a more quantitative phase, where the emissions from the Taylor cone would be analyzed by time of flight mass spectrometry.

3. Prospects of using this coaxial source as an ion emitter

Our original proposal had contemplated the possibility not only of forming small drops, but perhaps also of creating intense beams of ions from coaxial water-oil systems. Which one of these two possible modes of emission is favored remains to be clarified through a second phase involving mass spectrometric characterization. In the mean time, under a different research program, we have learned some relevant facts that illuminate the issue. Using room temperature molten salts (ionic liquids) we have discovered the existence of a regime of purely ionic emission, as well as a regime of high current emission (> 20 μA), mostly of ions. However, it appears that the high current regime (and possibly also the purely ionic regime) sets in as a result of resistive heating of the tip regio of the Taylor cone. If this were to be confirmed, heating would evidently lead to substantial increases in the vapor pressure of water, which would at some point tend to destabilize these coaxial jets. Hence, although it is possible that moderate levels of Joule heating will conceivably favor ion evaporation from water-oil tips, it is less likely that the high curents (~ 20 μA) observed in ionc liquids will be attainable by water-oil sprays.

4. Conclusions:

Water and other volatile liquids can be electrosprayed in a vacuum at flow rates small enough to attain conditions competitive with the best presently known colloidal propellants based on organic solvents. The advantages offered by coaxial electrosprays are considerable, certainly greater than envisioned at the beginning of this study. In view of these promising results we conclude that a systematic TOF-MS study of the propulsion characteristics of oil sheathed Taylor cones is warranted. There is almost no doubt that coaxial Taylor cones will be able to provide much better propulsion characteristics than any known alternative organic electrolyte.

Technical difficulties associated with the feed of the sheath liquid have impaired our progress beyond the qualitative findings just reported. But a new design for a practical feed is now available, and will greatly simplify future developments in this field.

5. References

M. Gamero-Castaño & V. Hruby (2001) "Electrospray as a source of nanoparticles for efficient colloid thrusters", Journal of Propulsion and Power, **17**, 977-987.

P. Lozano and M. Martinez-Sanchez, Experimental measurement of colloid thruster plumes in the ion-droplet mixed regime (submitted to AIAA J., July 2002). See also P. Lozano, Ph.D. Thesis, MIT, 2003

R. Bocanegra, J. Fernandez de la Mora and M. Gamero, Ammonium electrolytes quench ion evaporation in colloidal propulsion (submitted to J. Propulsion and Power, July 2002).

A. Barrero (2002) Private communication

6. Personnel

Graduate students: Mr. Ismael Guerrero. Performed most of the preparative experimental work, putting together the vacuum system and the liquid feed system

Postdoctoral visitor: Dr. Inigo Aguirre: Did the experiments with coaxial sprays in vacuo

PI: Supervised this work, and developed the final coaxial feed system based on pulled capillaries.

7. Interactions, transitions

No publications have resulted from this effort.

Results on the stability of water-oil Taylor cones were reported at the 2002 AFOSR contractors meeting (Colorado Springs).

Initial interactions with Busek Inc. (Dr. Manuel Gamero) led to their writing of a proposal that was not funded. In the mean time the main interest of most actors in this field has shifted to the use of ionic liquids. The coaxial technique is not sufficiently developed, and we have not succeeded at pushing it to a level suitable for more serious industrial participation. We believe this could be done if a comparable funding level were to be injected into a second phase (~$30,000).

Interaction with Professors Antonio Barrero (U. Sevilla) and Ignacio Loscertales (U. Malaga) and Martinez-Sanchez (MIT) has been maintained through the project.

8. Inventions

A new US patent application has been made under the title: Method to produce ions and nanodrops from Taylor cones of volatile liquids at reduced pressures (Juan Fernandez de la Mora inventor; assigned to Yale University). This application claims the benefit of priority to U.S. Provisional Patent Application No. 60/327,528, filed on October 5, 2001. Although the invention preceded conceptually the funding period, it has been brought to practice thanks to this grant.